Theoretical Gas Phase Chemical Kinetics

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Training in theoretical chemical kinetics

1. CEFRC – Summer School

   Ab Initio Theoretical Chemical Kinetics

2. Peng Zhang (Ed Law graduate student; now a CEFRC Fellow)

   Monomethylhydrazine decomposition

3. Franklin Goldsmith (Bill Green graduate student)

   Allyl + HO2

4. Mike Burke (Fred Dryer & Yiguang Ju graduate student)

   H2/O2 Combustion

Monomethyl hydrazine decomposition

- Monomethylhydrazine (MMH)
  - Diamine-based rocket fuel
  - Commonly used as bipropellant and monopropellant
  - Exothermically decomposes upon contact with either a hot surface or an oxidizer
- Thermal decomposition of MMH
  - Fuel stability and storability
  - Necessary components of mechanism of MMH oxidation
  - Have not been sufficiently studied
- Dominant reactions of MMH decomposition: NN and CN bond fission

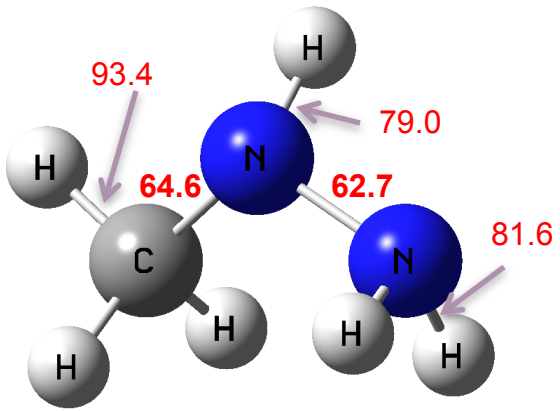
$$MMH \rightarrow NH_2 + CH_3NH$$

$$MMH \rightarrow CH_3 + NHNH_2$$

- Barrierless radical-radical recombination reactions

$$NH_2 + CH_3NH \rightarrow MMH$$

$$CH_3 + NHNH_2 \rightarrow MMH$$



kcal/mol

Potential Energy Surface

- On-the-fly Calculation of Interaction Potential

– aug-cc-pVTZ: accurate but too computationally demanding → cc-pVDZ and aug-cc-pVDZ were used

– Reacting fragments have fixed internal geometries

- Orientation-Independent Corrections
  - One-dimensional basis set correction
  - One-dimensional correction for geometric relaxation

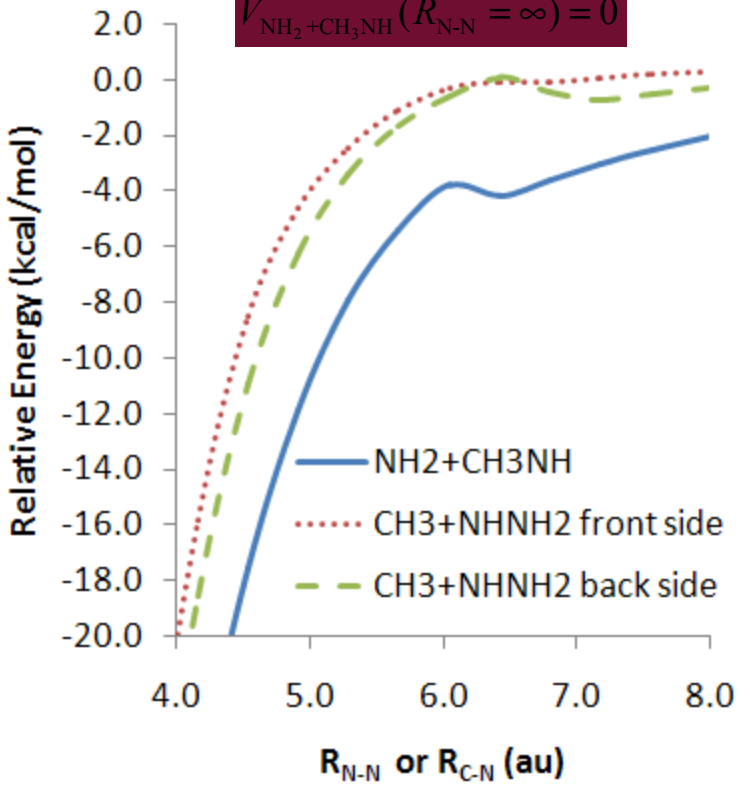
Basis set | Separation of fragments | Relative orientation | Reacting fragments have fixed internal geometries

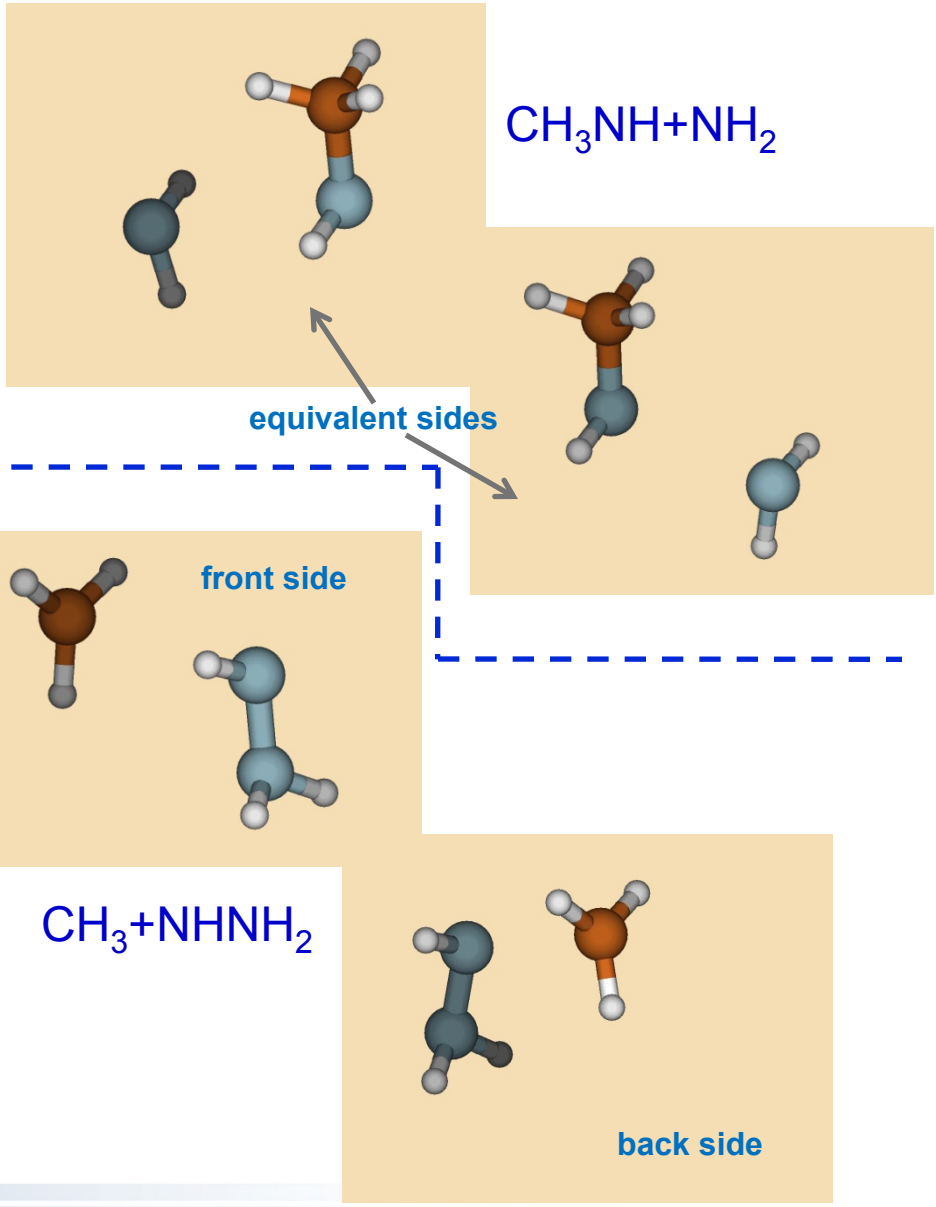
$$V = V_{CASPT2/ADZ}(R,\Omega;rigid)$$
$$+\underbrace{\left[V_{CASPT2/ATZ}(R,\Omega^*;rigid) - V_{CASPT2/ADZ}(R,\Omega^*;rigid)\right]}_{\text{basis set correction from CASPT2/aug-cc-pVTZ}}$$
$$+\underbrace{\left[V_{CASPT2/ADZ}(R,\Omega_e;relaxed) - V_{CASPT2/ADZ}(R,\Omega_e;rigid)\right]}_{\text{correction for relaxing of the internal structure}}$$

Potential Energy Surface

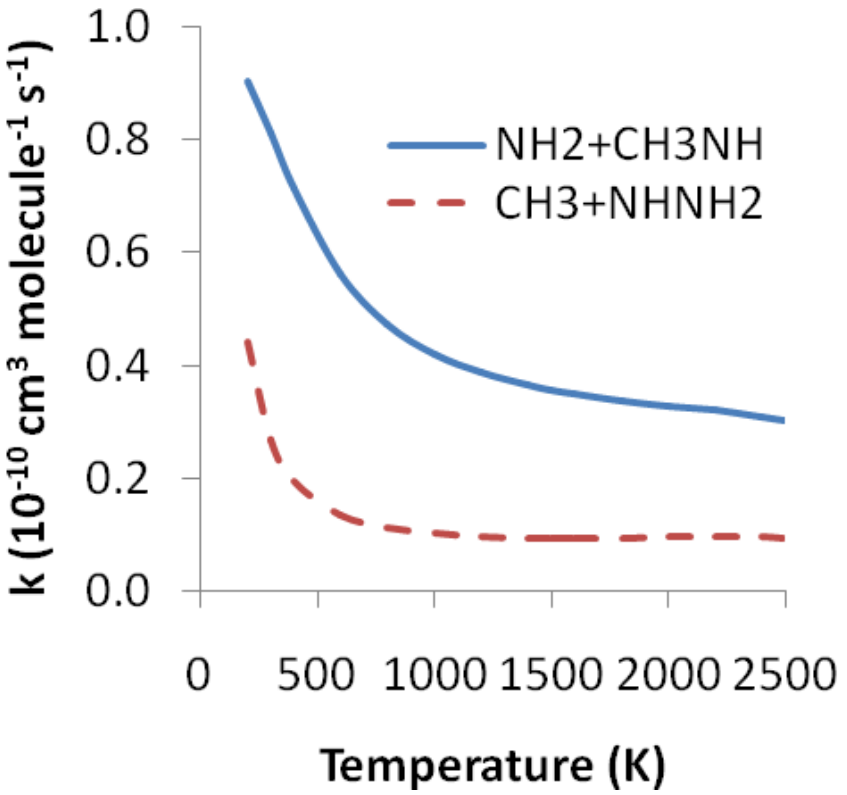
Potential curves

$V_{NH_2+CH_3NH}(R_{N\text{-}N}=\infty)=0$





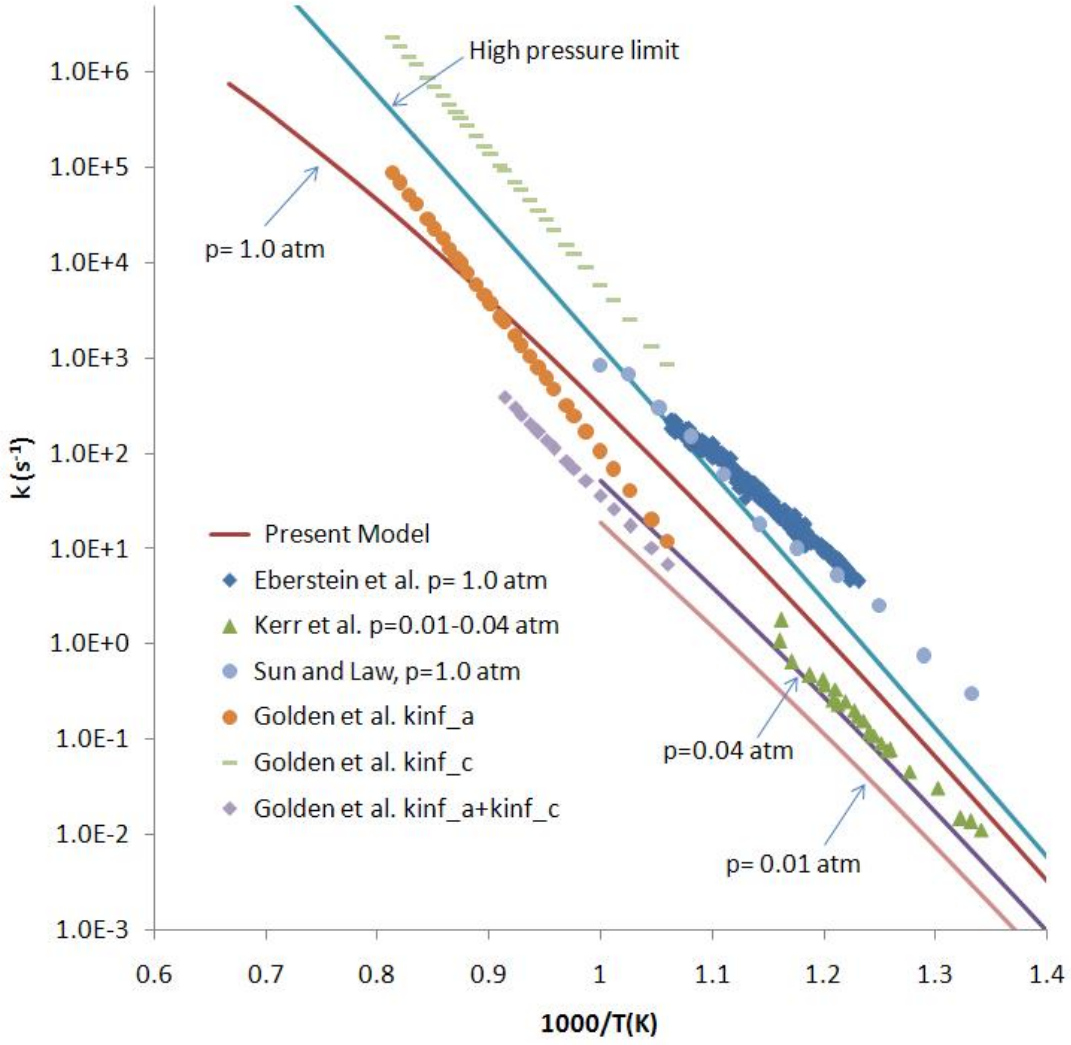
VRC-TST Capture Rates



$$k_{-1}^{\infty} = 8.34\times10^{-10}T^{-0.429}\exp(20.1/T)\ \mathrm{cm^3\cdot molecule^{-1}\cdot s^{-1}}$$

$$k_{-2}^{\infty} = 3.99\times10^{-12}T^{0.085}\exp(404.2/T)\ \mathrm{cm^3\cdot molecule^{-1}\cdot s^{-1}}$$

MMH Dissociation: Theory-Experiment Comparison



• Kerr et al (1963): the first-order rate coefficient for the homogeneous dissociation of NN bond of MMH.

– Very good agreement with the present theory

• Golden et al (1972): very low pressure reactor → complicated by gas-wall interactions

– Not appropriate for a direct comparison with the theory

• Eberstein et al (1965): total thermal decomposition rate of MMH

– Modeled by a mechanism containing 43 species and 160 reactions (Sun and Law 1007)

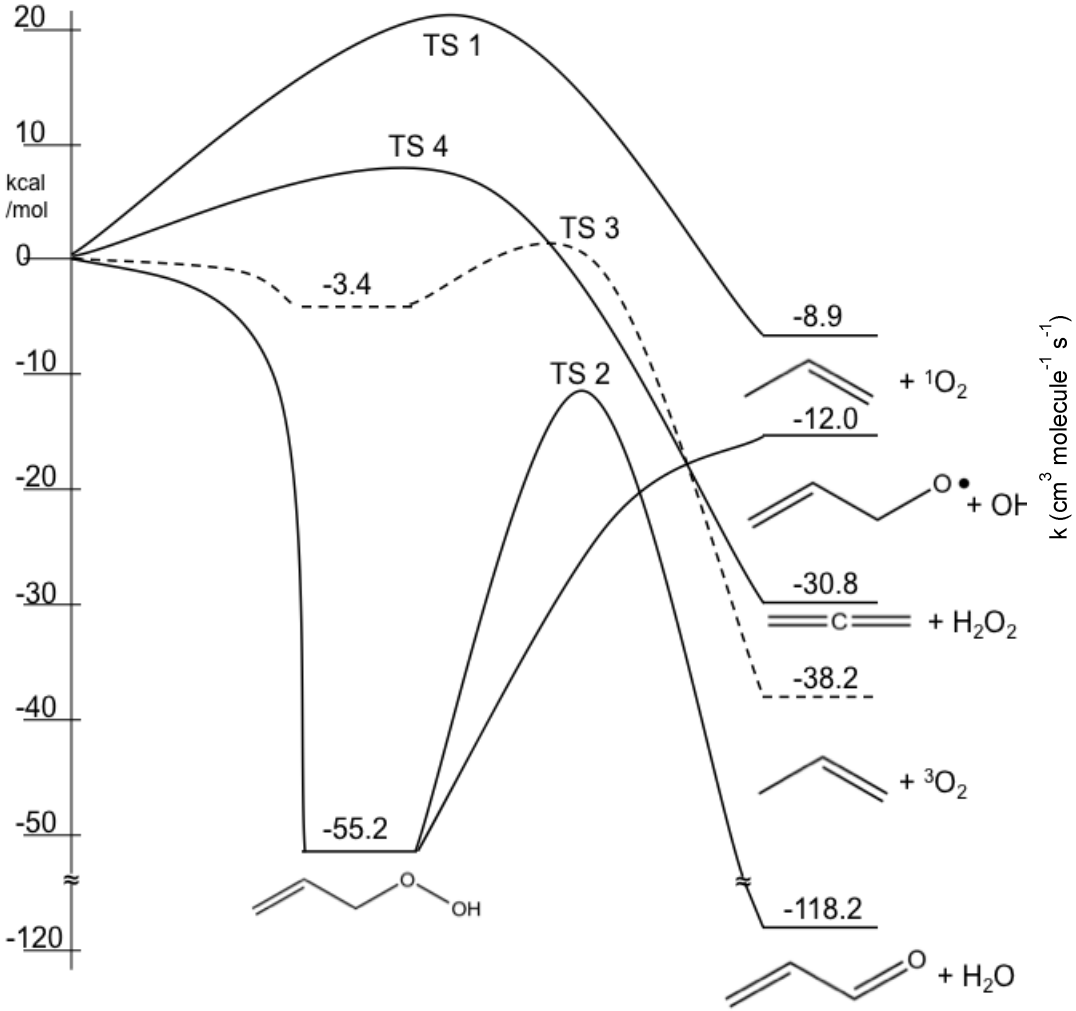
– Sensitivity analysis identified two qualitatively important reaction channels:

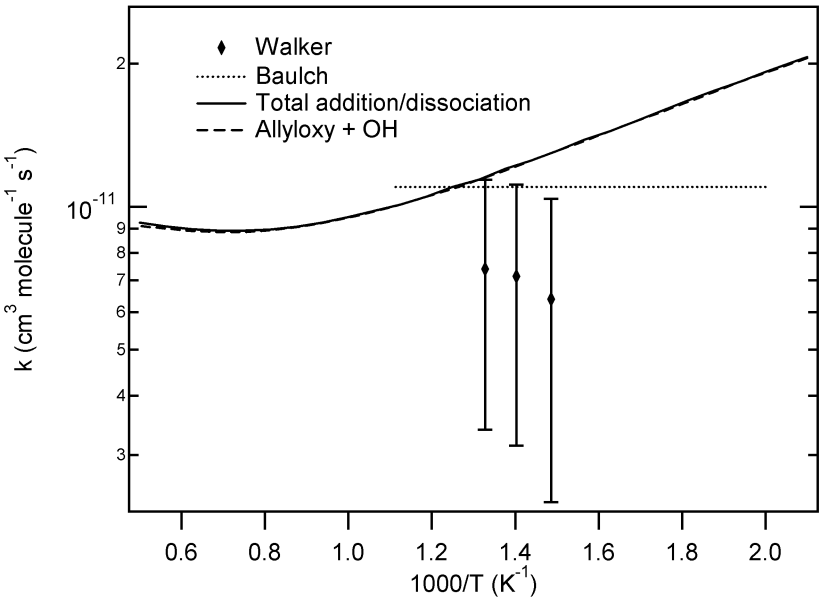
$CH_3NHNH_2 + CH_3 \rightarrow CH_3NNH_2 + CH_4$

$CH_3NNH_2 \rightarrow CH_3NNH + H$

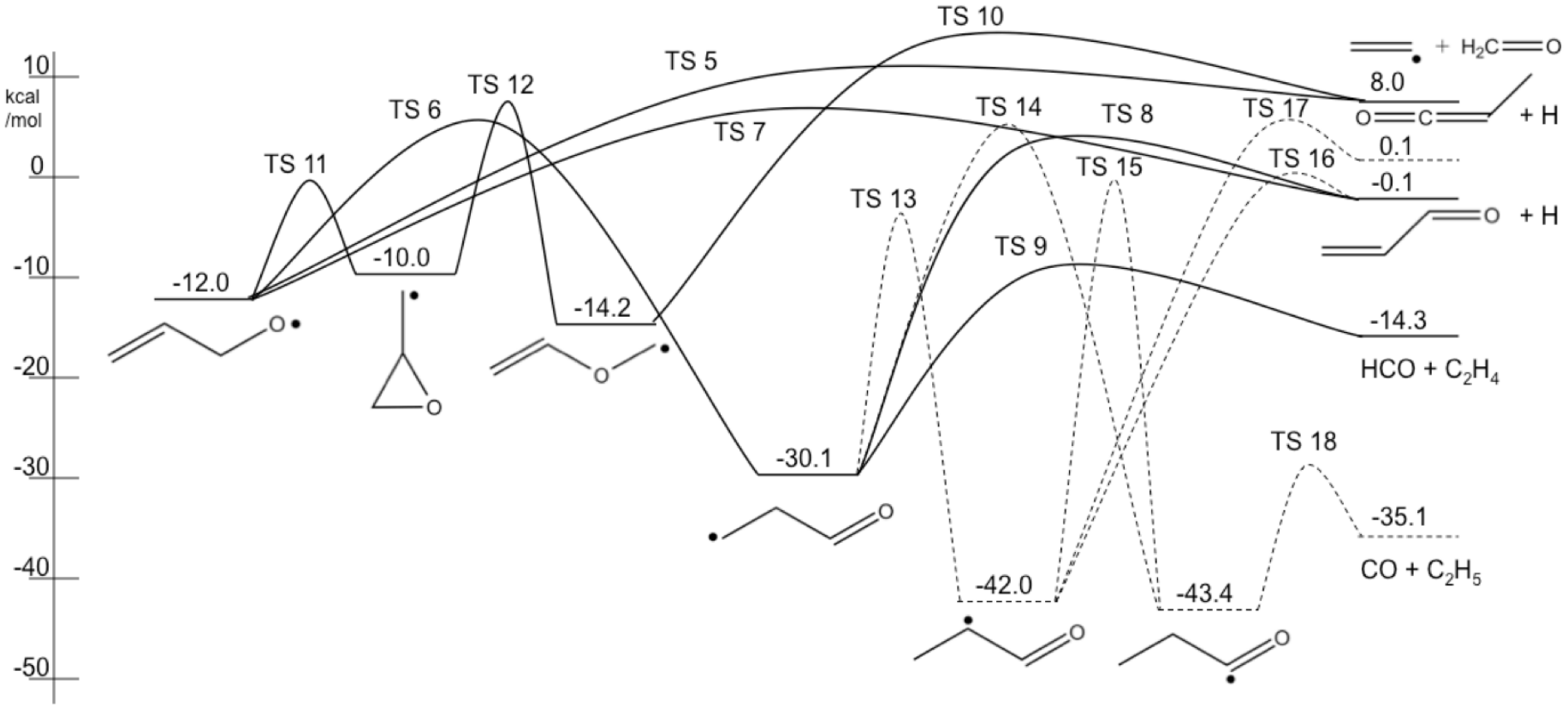
– Disagreement with the theory might be due to the absence of the two reaction channels:

Allyl + HO2


20
10
kcal
/mol
0
-10
-20
-30
-40
-50
-120
TS 1
TS 4
TS 3
TS 2
-3.4
-55.2
-8.9
-12.0
-30.8
-38.2
-118.2
+ $^1O_2$
+ OH
+ H_2O_2
+ $^3O_2$
+ H_2O
OH


Walker
Baulch
Total addition/dissociation
Allyloxy + OH
k (cm^3 molecule^{-1} s^{-1})
10^{-11}
2
9
8
7
6
5
4
3
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
1000/T (K^{-1})

Allyloxy Decomposition



Allyloxy Decomposition